Attachment D

must be capable of purification to a maximum impurity level of around 300ppm, and for transparent silica it should be purified to a maximum of about 30ppm. The presence of TiO_2 in the chemical analysis may indicate the presence of rutile, needles of which could cause problems in drawing tubing by producing bubbles. In semi-conductor products the presence of heavy metals, which act as conductors, would be deleterious.

Particle size for the silica feed is very much dependent upon the fusion methods — torch, resistor furnace etc. and sand ranging from 50–500μ can be used. The ratio of silica raw material to fused silica product varies from 1:1 to 3:1.

Typical analysis of US high purity quartz sand

	ppm	
Al	20.0	
Fe	0.5	
Na	0.4	
K	0.4	
Ca	0.4	
Li	0.4	
Mg	1.0	
Ti	1.0	
Max. retained on 50 mesh screen		2%
Max. through 140 mesh screen		5%

Microsilica

Essentially microsilica is not produced directly from a silica mineral but is formed as a by-product of ferro-silicon or silicon production. However, the final quality of the microsilica by-product can be controlled to some extent by ensuring the purity of the silica raw material (quartz) used to manufacture the primary product. Microsilica is recovered from the hot waste gases produced during ferro-silicon or silicon manufacture in the following manner. SiO vapour mixes with oxygen in the upper, cooler part of the furnace, oxidises to form SiO_2 and condenses in the form of microspheres of amorphous silica. After passing through a pre-collector and cyclone to remove coarser particles, the material is blown into and collected in specially designed baghouse filters. The resultant product consists of finely divided amorphous silica spheres with a particle size similar to that of tobacco smoke. Average particle diameter is of the order of 0.15 microns.

Microsilica obtained as a by-product of silicon metal manufacture possesses a higher silica content (94–98% SiO_2) than that obtained from ferro-silicon production (about 85–90% SiO_2). Subsequently, consistency of product quality to ±2% can be further achieved by blending. Because of its by-product status microsilica has a considerable economic advantage over silica produced by other chemical means. The average price for untreated microsilica grades varies from around £150–250 per tonne.

Typical chemical composition of microsilica

% by weight	*Refractory grade*	*Concrete grade*
SiO_2	94–98	85–96
Fe_2O_3	0.1–0.4	0.2–3.0
Al_2O_3	0.02–0.4	0.2–0.5
CaO	0.1–0.4	0.1–0.7
MgO	0.2–0.9	0.3–3.5
Na_2O	0.1–0.4	0.2–1.8
K_2O	0.2–0.7	0.4–3.5
C	0.2–1.3	0.4–2.3
MnO	—	—
LOI	0.05–2.5	0.7–4.0

Source: Concrete, October 1985

About 120,000 tpa of high quality microsilica is available for use, derived from silicon and ferro-silicon manufacture. The material is characterised by a very small particle size (average diameter 0.15μ), spherical particles, and a very high surface area (about 20 sq metres per g). These attributes combine to make microsilica a highly reactive silica product. Because of their size and shape particles are able to move between and around coarser particles, filling even the most minute spaces in any mixture. There are consequently several areas of application for which microsilica is particularly well suited.

Cementitious applications

In cementitious compositions the microsilica particles act as a superpozzolan as well as filler, converting less useful calcium hydroxide crystals into calcium silicate hydroxide gel binder. This results in an improved microstructure because of the denser pore structure, which in turn results in reduced permeability, increased durability, and higher strength. Bonding to aggregate and reinforcing materials increases and in fibre-reinforced products the fibre durability is also improved.

Glossary

Amorphous silica is often used with reference to the naturally occurring mineral tripoli which is mined exclusively in Illinois and Missouri in the USA. This is indeed a misnomer since tripoli is a microcrystalline silica in which no amporphous particles have been detected. True amorphous silicas include precipitated silica, fumed silica, silica gel, and glassy minerals such as expanded perlite. It also includes materials such as microsilica spheres which are obtained as a by-product from silicon and ferro-silicon manufacture.

- **Fumed silica** is an amorphous synthetic silica ie. it is not produced directly from a naturally occurring silica mineral, but is a chemically derived product. Fumed silica can be produced from the reaction of ferro-silicon with hydrochloric acid to produce silicon tetrachloride which is subsequently hydrolised in a flame of hydrogen and oxygen to produce silica. This product is also known as pyrogenic or colloidal silica. The cost of fumed silica (at about £4 per kg) is greater than that of microsilica which is essentially a by-product and commands prices in the region of less than £1 per kg. Fumed silica will be considered in the context of this article only in those areas of application which overlap with naturally occurring silicas.
- **Microsilica** will be used in the context of this feature to refer to the silica spheres obtained as a by-product of silicon and ferro-silicon manufacture. As such they will also be discussed alongside natural silica minerals since they are essentially obtained as a primary product from silica sand rather than being chemically derived. The term will not be applied to any naturally occurring silica mineral. In other literature microsilica products are also referred to as volatised, arc furnace, pyrogenic, and fume silica.

Precipitated silica is a synthetically produced amorphous silica obtained from the reaction of water glass (sodium silicate) with carbonic or sulphuric acid. The sodium silicate is prepared by heating silica sand which has been prereacted with caustic soda. The product is then diluted to produce water glass. Silica sand raw material requirements for this application specify a minimum 99% silica content, maximum 0.45% alumina, and maximum 0.1% Fe_2O_3. The size requirement is for 100% less than 20 mesh.

Pyrogenic silicas

A synthetic version of silica can be produced by an electric arc process with a charge of quartz and coke but apart from minor usage by *F. B. Goodrich Co.* in the USA and Degussa in West Germany, this process has not been a truly commercially viable one. The most important pyrogenic silicas are derived from silicon tetrachloride (also known as tetrachlorosilane), itself produced from silicon metal (or in some cases ferrosilicon) for which the starting raw material is lump quartz.

Fumed silica

Fumed silica is prepared by the high-temperature hydrolysis of silicon tetrachloride in a flame of hydrogen and oxygen. The resultant silica consists of very fine spherical particles of an even size (typically in the 7–20 nanometre range). Primary particles are often joined together in aggregates or chains and most importantly the outer surfaces are populated by hydroxyl ions.

When fumed silica is dispersed in liquid systems, its surface hydroxyl ions can link the individual aggregates into intricate, three-dimensional networks which result in thickening or gel formation. Since the linkages may be easily broken (by shear) and re-established the product is an excellent example of a thixotropic material.

When blended into powder systems, fumed silica works as an anticaking and free-flowing agent — since its fine particle size and high surface area enable it to cover the large particles of powder with a thin coating.

Other silicon-metal-derived products

Silicon metal provides the starting point for a number of high purity silicon compounds including silanes, silicones, fumed silica (described above), and semiconductor silicon. The intermediate product for most of these compounds is silicon tetrachloride (or tetrachlorosilane).

Silicones

The silicones, or polysiloxanes, are chemical polymers in which atoms of silicon and oxygen form the central chain (rather than carbon as in "conventional" organic polymers). In most silicones two organic groups — usually methyl ($-CH_3$) or phenyl ($-C_6H_5$) — are attached to each silicon atom. They range from oily liquids to rubbery solids and are stable toward heat, water repellant, chemically inert, and electrically insulating. Silicones are used as lubricants, hydraulic fluids, electrical insulators, and moisture-proofing agents.

The main manufacturing process involves the reaction between methyl chloride with powdered silicon metal powder (in the presence of copper/copper oxide catalysts) to produce a mixture of chlorosilanes, which are separated by fractional distillation. The different chlorosilanes, which have the general formula R_nSiCl_{4-n}, can then be polymerised by controlled hydrolysis.

Silanes

The silanes are a series of covalently bonded compounds containing silicon and hydrogen with the general formula Si_nH_{2n+2} and the simplest member is monosilane, SiH_4. The silanes are structural analogues of the saturated hydrocarbons but are much less stable. Pure silanes can be made by the reaction between magnesium silicide and acid or between silicon tetrachloride and lithium aluminium hydride; they are highly unstable and burn or explode on contact with air. The chlorosilanes are important intermediate compounds and may also be used in direct application to impart water repellancy to other materials.

Semiconductor silicon

The purification process to convert silicon metal into super-pure semiconductor silicon begins with the production of an intermediate compound such as trichlorosilane ($SiHCl_3$) or tetrachlorosilane ($SiCl_4$) which is then purified by fractional distillation. The purified distillate is then pyrolytically decomposed in an atmosphere of hydrogen to yield super-pure silicon metal and hydrochloric acid:

$$H_2 + SiHCl_3 \rightarrow Si + 3HCl$$

The polycrystalline silicon thus formed is converted to single crystal by the Czochralski or floating-zone method.

Table 5. Typical properties of synthetic silicas

	Silica gel	*Pptd silica*	*Pptd silicates NaAl*	*Pptd silicates Ca*	*Fumed silica*
SiO_2 %	99.5	98.0–99.5	82	78	99.8 min
Na_2O %		0.2–1.0	9	2	
Al_2O_3			9		<0.05
CaO				18	
Fe_2O_3 %	0.01	<0.03	<0.03	<0.03	<0.003
SO_3 %		0.1–0.8	0.5	0.5	
LOI	3–15	3–7	6–12		1–3
Surface area BET, m^2/g	250–850	25–300	25–100		50–400
Average particle size (nanometers)	5–20	5–60	5–30		5–50
Pore diameter (angstroms)	20–200	>800			
Specific gravity	2.0	2.0	2.1		2.2
pH	3–8	5–9	10–11		3.6–4.3
Whiteness %		97	97		

Sources: Crosfield Chemicals, Degussa, Rhône-Poulenc, Cabot Corp.

Comparison of cementitious materials available in the UK

	Microsilica	OPC	PFA	GGBFS
Chemical (% by weight)				
SiO_2	92.0	20.0	50.0	38.0
Fe_2O_3	1.2	3.5	10.4	0.3
Al_2O_3	0.7	5.0	28.0	11.0
CaO	0.2	65.0	3.0	40.0
MgO	0.2	0.1	2.0	7.5
Na_2O+K_2O	2.0	0.8	3.2	1.2
Physical				
Surface area (m^2/kg)	15–20,000	350–500	300–600	300–500
Bulk density (kg/m^3)	200–300	1300–1400	1,000	1,000–2,000
Specific gravity	2.20	3.12	2.30	2.90

OPC ordinary portland cement; PFA pulverised fuel ash.
GGBFS ground granulated blast furnace slag.
Source: Elkem literature.

There is currently no British Standard for microsilica or microsilica concretes. However ASTM C618, which presents the requirements for fly ash and raw or calcined natural pozzolan used as mineral admixtures in portland cement concrete, is being updated to include microsilica. In Norway and Canada, where the bulk of microsilica is produced, standards do exist (NS 3050:1976, NS3474:1978, and A23.SM:1981). Some recommendations for microsilica have been derived from the British Board of Agrément Certificate.

SiO_2 content	85% minimum
Alkali content as Na_2O	2% maximum
Carbon content	2% maximum
% passing 45μ sieve	99% minimum
Solid content of slurries	50%±2%
pH of slurries	5.5±1

Overall, microsilica can offer a number of beneficial effects to concrete mixes including — total suppression of alkali silica reaction, reduction of permeability, sulphate resistance, reduced chloride ion penetration from 50% to 100%, corrosion inhibition, reduced carbonation, greatly improved freeze-thaw durability, improved workability and pumpability, increased chemical and abrasion resistance, and increased compressive, flexural, and tensile strengths.

Polymer applications

Microsilica particles function as effective reinforcing fillers in extruded polymer products, serving to improve their impact resistance and stiffness. Special microsilica products with matched chemical additives are also produced which contribute to a smoother production process and increased productivity.

Refractory applications

Only the highest microsilica grades produced from silicon metal manufacture are used in refractory applications because f its higher price and limited availability. These grades are used in refractory concretes made from calcium aluminate cements and in other refractory materials eg. castables and bricks, where they improve the hydraulic and ceramic bonding of these products thereby enhancing other properties Increasingly, refractory castables containing microsilica are replacing refractory bricks in many areas. Whilst conventional castables have limitations relating to their physical, mechanical, and thermal properties because of their water and calcium contents, the addition f microsilica reduces the amount of calcium aluminate required and consequently the water content. As a result microsilica castables can achieve strengths some three or four times higher than conventional materials. The new range of castables, which have microsilica contents varying from 2% to 12% by weight and calcium aluminate contents of 0–10% by weight, possess high mechanical strength, high resistance to mechanical abrasion, excellent resistance to thermal shock because of the even expansion characteristics, low shrinkage due to low water content, and a low apparent porosity.

Microsilica is additionally being used in monolithic linings and precast shapes and allows their production by new techniques thereby eliminating the need for firing before installation. In high alumina bricks the addition of microsilica reduces the need for water, its high reactivity improves the ceramic bonding so that firing temperatures can be lowered by about 100–150°C, and the dense packing improves product resistance to chemical and abrasive wear. Microsilica improves adhesion in castables and minimises rebound loss when used as a gunning refractory material.

Overall, the high strength of microsilica-based castable refractories makes it possible to considerably reduce the lining thickness in most kilns, furnaces, boilers, and preheaters. Despite being a relatively new additive material in the refractories industry a large number of applications have been found in the steel and foundry, cement, petroleum and petrochemical, ceramic, glass, and pulp industries. Additionally, special application areas have been identified eg. in incinerators and power station boilers.

Other uses

The high reactivity of microsilica is found to give economic benefits in the production of various silicates whilst it is also used as coating powders, insulating powders, aids to catalyst support systems, and for selective adsorption of ions in the chemical industry.

Filler and extender applications

Silica in its finest forms, as a flour, microsilica, precipitated, and fumed finds application in reinforcement filler and extender applications. Here the particle size and surface area of the silica are two of its most important attributes. Tripoli is produced in a variety of grades ranging from 99% less than 74μ to 99% less than 10μ and there is also the likelihood of even smaller grades being produced. Its purity is high, averaging about 98–99% SiO_2, 0.1–1% Fe_2O_3 according to the source (Missouri-Oklahoma "rose" or "cream" tripoli has the higher iron content whilst the Illinois white variety has the lower), and less than 1% alumina. The ultimate particle size is sub-micron but tripoli particles tend to agglomerate to form porous aggregates. Precipitated silica similarly is composed of aggregates of sub-micron particles (average diameter 0.019μ) which agglomerate to form larger clusters. Silica content of the grades varies from 87% to 97.5%. Precipitated silicas currently sell for around $0.4–0.5 per lb. Fumed silica, also found in agglomerated form, has particles with nominal diameters ranging from 0.014–0.007μ and a silica content averaging more than 99.8%. The cost of fumed silica is around £4 per kg.

Plastic

Silica flour and tripoli are used to impart flexural and compressive strength to plastics. In addition, their low oil absorption, wettability, and rapid dispersion allow high loading in most compounds. Silica additions improve dimensional stability and improve resistance to thermal shock. One problem identified with the use of these products, however, is wear on extruding nozzles and moulds. It is anticipated that finer gradings should overcome this drawback. The excellent dielectric properties of tripoli also make it suitable for plastics used to encapsulate electronic components.